International Journal of Environment, Ecology, Family and Urban Studies (IJEEFUS)
ISSN(P): 2250-0065; ISSN(E): 2321-0109
Vol. 5, Issue 5, Oct 2015, 29-42

HEAVY METALS CONTAMINATIONS IN IRRIGRATED VEGATABLES, SOILS, RIVER WATER: A COMPRESSIVE STUDY CHILMARI, KURIGRAM, BANGLADESH

MIR T. RAHMAN[1], ABU L. M. E. ZIKU[2], TASRINA R. CHOUDHURY[3], JASIM U. AHMAD[4]&M. ABDUL MOTTALEB[5*]

[1,2,4]Department of Chemistry, Jahangirnagar University, Savar, Dhaka, Bangladesh

[3]Chemistry Division, Atomic Energy Centre, Dhaka, Bangladesh

[5]Center for Innovation and Entrepreneurship, Department of Natural Sciences,

Northwest Missouri State University, University Drive, Maryville, Missouri 64468,USA

Submitted: August 6, 2015; Accepted: August 10, 2015; Publication certification: October 31, 2015.

ABSTRACT

Metal contaminations and exposures are recognized as a risk to human health because of consumption of elements through vegetables and environment.Fourteen composite samples include five different vegetables, five soils and four Brahmaputra River water collected from the Chilmari, Kurigram, Bangladesh were digested and examined, in this study.Quantifications of heavy metals from the composite specimens were made using Atomic Absorption Spectrophotometer methods (AAS) against standard calibration plot.The frequency of metals were observed in the order of soil > vegetable > waters.Soils samples provided higher concentration than vegetables and water specimens for nine metals such as Pb, Cd, Cr, Cu, Fe, Mn, Zn, Ca and Mg.On the other hand, increasing concentrations of Co, Ni, Na and K were observed in vegetables compared to soils and waters.The lowest concentrations of metals were received from water samples.The Fe, Cr, Ni and Mn concentrations exceeded the approved admissible levels in vegetables and/ or soils specimens at least 1 to 2 orders of magnitude and rests were within permissible limit.

KEYWORDS: Heavy Metals, Irrigated Vegetables, River Waters, Soils

INTRODUCTION

Many elements are essential nutrients for growth and survival of humans and other organisms.Although important, the metal nutrients requirements lie in narrow range and severe imbalance of elements proportions may cause an exposure to elevated concentrations that may induce to death of fish and serious sickness to human (Sharma et al. 2009; Agbozu et al. 2007).As a result, investigation of major, minor, toxic and trace elements in biological, agricultural produces andEnvironmental matrices has gained a distinct interest because of the critical role in human health as well as the ecosystems (Zvinowanda 2009; Zaidi et al. 2002).Consequently, these issues draw special attention of global scientists to investigate the metal nutrients in fruits, vegetables, soils, waters and surrounds environments and to correlate the metal contaminations routes in dietary food chain (Ajasa et al. 2004; Shrivas and Jaiswal, 2013; Randjelovic et al. 2014).

Studies have shown the transfers of nutrients and toxic metals including Pb, Cd and As from landmass to the sea by a small Mediterranean river (Nicolau et al. 2006).River systems are major routes for transportation of metals (Miller et al. 2003) and trace elements may become significant pollutants of many small river banks and lakes (Dassenakis et al.

1998; Quraishi et al. 2010).More studies suggested that the behavior of metal in waters is a function of the substrate sediments, the suspended solid composition and the water chemistry (Harikumar et al. 2009; Shrestha et al. 2007).In the course of transport, the trace metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena (Akcay et al. 2003; Ghani and Elchaghaby 2007], which affect their behavior and bioavailability.Hobbelen et al. (2009) demonstrated that the accumulation and distribution of hydrocarbons, trace metals and chlorinated compounds in soil, water and the environment are increasing at an alarming rate causing deposition and sedimentation in water reservoirs and affecting aquatic organisms and sea weeds.

The observance of metals availability in surface is primarily derived from rock, amended soil, precipitation and river systems. Soils are variably contaminated with metals as a result of human activities including transportation, construction, manufacturing, fossil fuel combustion, and emissions (Alloway 2004; Biasioli et al. 2007).Consequently, soils can be contaminated, moderately to severely, with heavy toxic metals such as lead, cadmium, and mercury and most likely to pose some hazard for garden foods and human health (Alloway 2004; Spliethoff et al. 2014; Stilwell et al., 2008). Their long-term deposition may reduce soil buffering capacity and cause soil and groundwater contamination (Arora et al. 2008).The trace metal contaminations grow every year, presenting a serious problem for human health and a grave danger to the atmosphere (Marin et al. 2001).

Metals are not biodegradable and they may accumulate up in food chain from soil metals during the growth and processing.Heavy metals are one of the common types of contaminants that can be found on plants, fruits and vegetables salads (Husaini et al. 2011; Arif et al. 2011; McBride et al. 2014).Contamination of fruits and vegetables with metals may be due to irrigation with contaminated water, metal-based pesticides and fertilizers, high traffic areas, industrial emissions, transportation, the harvesting process, and storage (Sachan et al. 2007).In addition, fruits and vegetables may be contaminated when farmers wash the products with polluted wastewater before bringing them to the supermarket – this situation may happen especially in South Asian developing countries herein Bangladesh where fresh water resources are limited for framing land and farmers.Sharma et al. (2009) reported that transportation and marketing systems of vegetables play an important role in elevating the contaminant levels of heavy metals that may pose a threat to the quality of the vegetables.Mor and Ceylan (2008) have observed higher levels of Pb and Cd in the vegetables grown in traffic areas than those found in rural areas.Vegetables grown at contaminated sites could take up and accumulate metals at concentrations that are toxic (Wright 1991).Although some metals are micronutrients, they are toxic in high concentrations (Zvinowanda 2009; Zaidi 2002; Wright 1991].Increased heavy metal concentrations may lead to high amount of human intake, causing serious illness (Sharma et al. 2009; Radwan and Salama 2006; Chojnacka et al. 2005).

In the present study, the ChilmariUpazila, Kurigram district, Bangladesh has been selected.The Chilmari is a non-industrial and non-traffic zone which drives the economic power of whole Kurigram district through farming land activities and agriculture commodities.Chilmari farmers utilizes heavy chemical fertilizers, pest controls in farming lands to grow numerous plants, fruits and vegetables in the soils and also irrigates the Brahmaputra river waters for their cultivation.Finally, agriculture produces are taken and transported to the local supermarkets as dietary food.As plants establish the basis of the fruits and vegetables, some concerns have been raised about the possibility of toxic concentrations of certain elements being routed from plants to dietary food (Peralta-Videa et al. 2009).Moreover vegetables, consumed raw or cooked, may pose more hazards because the cooking process is ineffective that may reduce metal concentrations (Perello et al. 2008).Heavy metals may also deposit on the surface of the fruits and vegetables, or may be taken up by the

crop roots and incorporated into the plant tissue.Metal deposited on the surface of the crop can often be washed off by consumers prior to their consumption.In view of these facts, we analyze the concentrations of different heavy metals in waters, soils and fruits/vegetables specimens collecting from the Chilmari area, Kurigram district of Bangladesh.Farmers pumped the river water to the soils where fruits/vegetables were grown.The objective of research is to investigate all samples results - how Brahmaputra river waters and farming soils contribute metals concentrations in growing of fruits/vegetables and to screen how amount consumption of heavy metals are occurring due to eating of the fruits/vegetables grown in the sampling area.

MATERIALS AND METHODS

Chemical and Equipment Used

The Individual standards of AAS grade stock solution 1000 mg L^{-1}such as Pb, Cd, Cr, Cu, Co, Ni, Fe, Mn, Zn, Ca, Mg, Na and K were purchased from Spectro Pure, USA.The working standard solution was prepared by diluting the stock solution of single element with ultra- pure water.Supra pure HNO_3 was obtained from E. Merck, Germany.All other chemicals were extra pure or supra pure received from E. Merck, Germany. Flame and graphite furnace atomic absorption spectroscopy (AAS), Varian Analytical Instruments, Models AA DUO 240 FS and AA 280 Z were used in this study.

Description of Study Area Secletion and Sampling Station

The study site was selected an area called ChilmariUpazila under Kurigram district in Bangladesh. Chimari area of Kurigram district is not treated as industrial zone, but plays a dominant role in economic growth of the district.Although the Chilmari is not an industrial zone, it drives the economic power of the whole district through farming land and agriculture supplies and commodities, where heavy utilization of chemical fertilizers and the Brahmaputra river waters are evident.

In brief description of the sampling sites, Chilmari and Kurigram district are under Rangpur Division in the northern region of Bangladesh along the border of India.The area of this district is 2,245.04 km^2 and population is 21,50974 (2011 national population census).It is located at 25.75^{o}N 89.66^{o}E and surrounded by Cooch Behar district of India in the North, Gaibandha district of Bangladesh in the South, Assam state of India in the East and, Lalmonirhat and Rangpur districts of Bangladesh in the West. From the ancient time, Kurigram is a land of agriculture and produces rice, jute, wheat, tobacco, potato, vegetables etc. for driving the economy of the Kurigram district.During winter season the ground water level usually goes down, farmers use the Brahmaputra river water in irrigation to cultivate high yielding varieties of rice and other crops to keep economy sustainable. Several cold storages add value to the economy of this district by preserving agricultural produces during summer season.As the sampling area is not an industrial zone, metals contamination in foods and soils in the area have not been examined yet.Thus monitoring and have some primary data of the metal concentrations in common edible foods/vegetables and in vegetables growing soils where the chemical fertilizers, the river water and petrol or diesel engine/boat invariably used would be scientific and public benefits.

Sampling Period, Sampling of the Samples, Sample Preparation and Analysis

Water, soils and vegetable specimens were collected on March 19, 2012 at the end of winter season when fruits/vegetables were mature.Figure 1 shows the samples collection sites and sampling points in the study area.

Water Samples

The water samples were collected from four different stations. The distance between sampling point was about

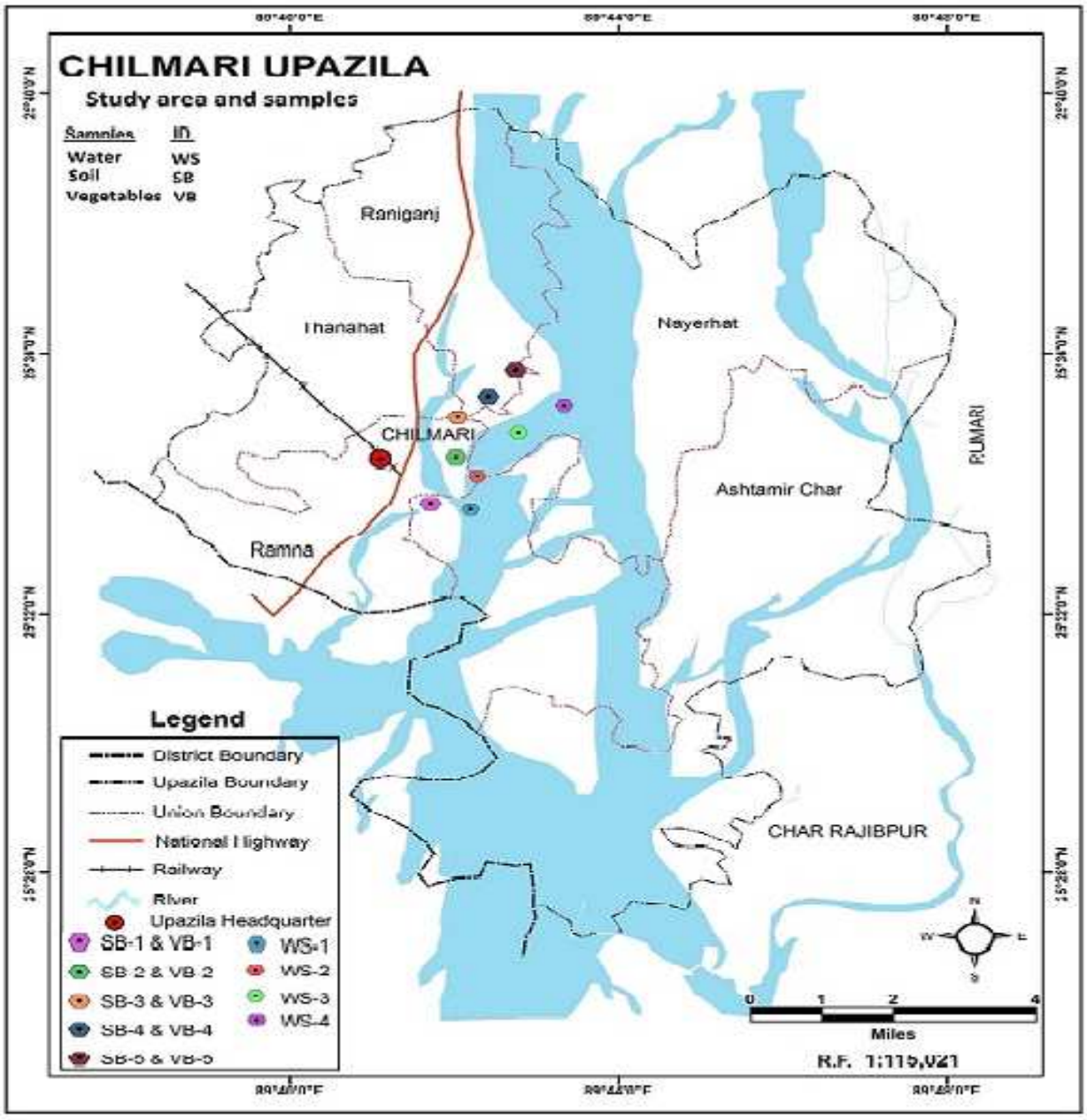

Fig. 1. A schematic map of study site and sample collation point in the Chilmari area of Kurigram district in Bangladesh.

1 km. The sampling stations were marked as WS-1, WS-2, WS-3 and WS-4 (Fig. 1). Three liters water samples were grabbed from each sampling station approximately 2 m depth from the surface of the water. The standard water sampler (Hydro Bios, Germany) were used with six pre-cleaned 500 mL volume polyethylene bottles to collect the water from each

sampling site. Then waters from six bottles (6x500 mL=3L) were mixed together to obtain a composite sample. Followed the composites were filtered through 0.45 µm membrane filters. Ultra-pure nitric acid was added to bring down the pH to <2.0 and stored the samples at 4°C in sampling kits and shipped to laboratory for heavy element analysis.

Soil Samples

Fifteen top-soil samples were collected from 5 to 20 cm depth from five different vegetable fields/stations using a Teflon coating knife in this study.The distance between each sampling station was about 100 m.Three replicates top-soil samples were grabbed from each sampling station. Approximately 3.0 kg (3 x 1000.0 g) of the samples were collected and immediately transferred into three new individual zip lock bags identifying with appropriate sample number, sampling location using a permanent marker. The collected soil samples were air dried for several days in Pyrex Petri dishes and then oven dried at 105 ^{o}C to attain a constant weight. Followed the samples were grounded in mortar and screened through a 2.0 mm sieve to obtain a homogeneous powder. The homogeneous powders of three replicates from each sampling station were mixed together uniformly and prepared a composite representative sample. Thus total five representative samples were prepared and stored in air-sealed cleaned plastic vials inside desiccators for further analysis. The samples were identified as SB-1 corresponded to Gourd field soil, SB-2 for Papaya field soil, SB-3 forKacha Kala(one kind of Banana) field soil, SB-4 for ChiniChampa Kala (one of kind of Banana) field soil and SB-5 for Bean field soil.The names of soil sampling fields that corresponded to the vegetables fields are presented in Table 1.

Table 1: Information of Vegetable and Soil Specimens Grabbed from Sampling Area of Chilmari, Kurigrum for this Study

Vegetable Samples					Soil Samples	
Sample ID	**Local Name**	**English Name**	**Scientific Name**	**Family Name**	**Sample id**	**Name of Sampling Locations**
VB-1	Laou	Gourd	*Lagenaria vulgaris*	Cucurbitaceae	SB-1	Gourd field soil
VB-2	Papaya	Papaya	*Carica papaya*	Caricaceae	SB-2	Papaya field soil
VB-3	Kachakala	Green Banana	*Musa paradisiaca*	Musaceae	SB-3	Boanana-Kacha Kala field soil
VB-4	ChiniChampakala	Banana	*Musa paradisiaca*	Musaceae	SB-4	Banana-ChiniChampa Kala
VB-5	Shim	Bean	*Lablab purpureus*	Papilionaceae	SB-5	Bean field soil

Vegetable Samples

Edible part of five selected varieties of vegetables shown Figure 2 were collected from matured vegetable plants using Teflon coating knife from the specified sampling sites/stations described in the earlier section.The sampling points were approximately 100 m away from each other.At least 200.0 g of each vegetable samples listed in Table 1 were collected from the same soil sampling fields and then transferred to zip lock bags. The specimens were marked appropriately for identification. Immediately after collection, samples were shipped by overnight delivery to the Atomic Energy Center Laboratory, Dhaka, Bangladesh.Followed the collected vegetable samples were thoroughly washed with fresh water to remove the adhering dirt and finally rinsed with deionized water. The samples were then air dried covering with clean cloth to avoid contamination of heavy metal from air and then oven dried in an oven at temperature of 70^{o}C to obtain a constant weight. Oven dried samples were grounded by using a glass mortar and passed through a 1.0 mm sieve to

obtain homogeneous power. The homogeneous powered samples were then stored in air-tight plastic vials inside a desiccator for further analysis.

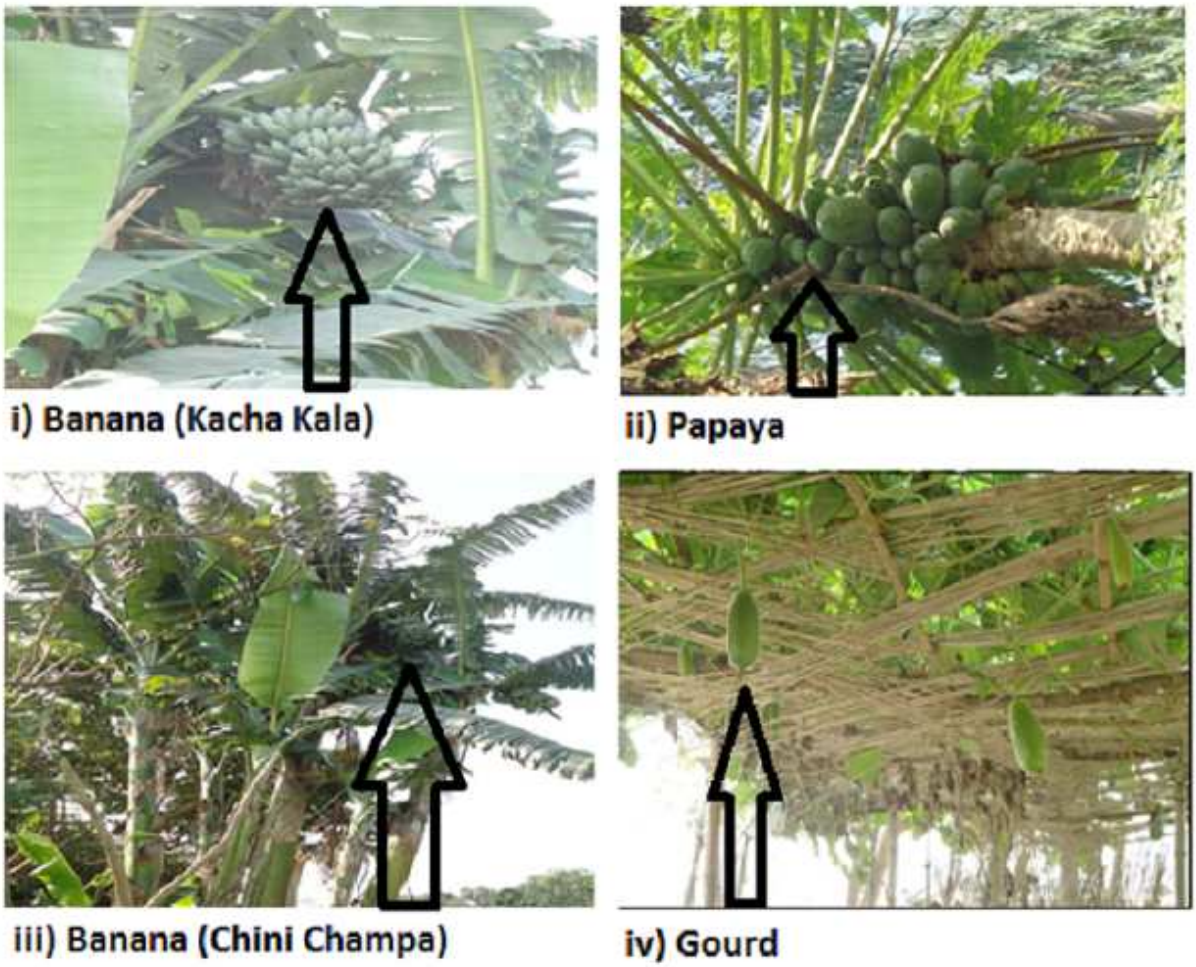

Fig. 2. Fruits and vegetable samples used in this study.

Digestion of Soil and Vegetable Samples for Metal Content Analysis

To determine the concentration of metals in the soil and vegetable, aliquot amount (about 0.1 g) of the ground specimens were taken in a XP vessel where 6 mL of concentrated HNO_3 was poured. Samples were then digested in a microwave accelerator reaction system (Model No: MARS 5) following US EPA procedure 3051A. Briefly, a representative sample of up to 0.5 g was digested in 10 mL of concentrated nitric acid for 10 min using microwave heating with a suitable laboratory microwave unit. The sample and acid were placed in a fluorocarbon (PFA or TFM) microwave vessel. The vessel was capped and heated in the microwave unit. After cooling, the vessel contents were filtered, centrifuged, or allowed to settle and then diluted to volume of 10 mL with de-ionized water in a 10 mL volumetric flask. Triplicates measurements were performed.Finally the samples were examined with AAS for metal estimation.

Metal Determination

Triplicates analysis were performed to determine heavy and trace metals in both water and sediment specimens

collected from each sampling station and period. Flame and graphite furnace AAS were employed. The metal standards prepared were checked with standard reference material obtained from National Institute of Standards and Technology (NIST), USA before each metal analysis and the deviation was found to be insignificant. Average values of three replicates were taken for each determination. Operational conditions were adjusted to yield optimal determination. Quantification of metals was based upon calibration curves of standard solutions of metals.

Calibration Curve and Quality Assurance/Quality Control

Known concentrations of each reference standard solution were used to prepare calibration levels. Calibration curves were prepared for all target elements using at least three and or four different concentration levels of each standard solution. Coefficient of variation (R^2 value) derived from statistical regression analysis exceeded 0.9995 for all elements. Individual calibration curve was used to determine the concentrations of each element/metal. Detection limit of each target elements/metals were observed and tabulated in Table 2.Quality assurance includes procedural blanks which were used throughout sample preparations to evaluate contamination from reagent, container, etc. No contamination was detected in the blanks. Procedures for sample preparations and experiments were validated by carrying out all operations in triplicate.Moreover standard reference materials were accounted whenever needed.

Table 2: Limit of Detection of Target Metals in Water, Soil and Vegetable Samples Analyzed by AAS

Target Metals	Water (Ug/L)	Soil (Mg/L)	Vegetables (Mg/L)
Pb	20.0	2.333	0.701
Cd	3.0	0.233	0.071
Cr	4.0	1.933	0.581
Co	3.80	1.266	0.380
Cu	2.40	0.800	0.242
Ni	3.70	1.233	0.370
Fe	3.90	1.300	0.390
Mn	1.90	0.633	0.191
Zn	0.67	0.223	0.067
Ca	14.6*	4.866	1.460
Mg	0.24*	0.080	0.024
Na	0.23*	0.076	0.023
K	1.76*	0.586	0.176

* represents unit as mg/L

RESULTS AND DISCUSSIONS

Brahmaputra River waters have been used to cultivate fruits/vegetables in the farming lands at Chilmari area of Bangladesh.In this study, fruits/vegetables, soils and water samples collected from Chilmari location (Fig. 1) have been used to determine the heavy metal concentrations in the specimens. Fourteen composite samples comprising of four waters, five soils and five fruits/vegetables were employed in this investigation.These primary results will generate the interest of researchers in absence of accessible metal concentration data for fruits/vegetables, soils, Brahmaputra River water in Chilmari site.

Water Samples Analysis

The river water used to grow the vegetables was composited and analyzed by AAS for determination of metals including Pb, Cd, Cr, Cu, Co, Ni, Fe, Mn, Zn, Ca, Mg, Na and K.Table 3 compares the concentrations of target metals between composite water samples and drinking/irrigation water. In general it can be seen that the metal concentrations received from the composite water samples are well below than standard permissible limit approved by the Department of Environment and Bangladesh Environment Management.The metals Pb, Cd, Cr and Co were not found to be detected in four water composite specimens above the detection (Table 2) except the WS1 composite which was collected from sampling station WS1 (Fig. 1) andprovided Pb concentration 37 ug/L.The observed Pb concentration was approximately 2 to 3 times lower than drinking or irrigation water permissible limit.The Cu, Ni, Fe, Mn and Zn concentrations were observed as 3.9 – 11.1, 3.8 – 18.4, 281 – 506, 5.1 – 24.8 and 10.1-22.8 ug/L in four composite samples and these values are approximately 10 to 100 times lower than admission levels of corresponding elements.The concentrations of Ca, Mg, Na and K ranged from 19.2 – 20.5, 4.9 – 6.8, 4.5 – 50.8 and 1.8 – 2.96 mg/L, respectively, were obtained in the water samples and these elements are considered to be most essential and no comparison was made in absence of standard limit availability.The water samples collected from different spots of the river and analyzed indicate that the thirteen target metals concentrations were below of the standards admissible limits.The average concentrations of heavy metals (macro- and micro nutrients) level were in the order of Fe > Na > Ca >Mn> Zn > Mg > K and trace toxic elements were Ni > Cu.Previously our research group reported the heavy and trace metals levels in Passur River water of Sundarban Mangrove Forest, Bangladesh (Rahman et al. 2011) and the values were higher than the concentration observed in Brahmaputra River water (Table 3).Khan et al., 1998 reported the concentrations of Pb, Zn, Fe, Cu, Ni, Cr in the Ganges and Meghna River waters ranges from 12.0-431.0, 71.0-675.0, 1160-12720, 2.4-3.4, 1.0-339.0, 15.0-491.0 ug/L respectively.These literature values are approximately one order magnitude higher except Cu while compared with present results.These suggest that Brahmaputra River waters are less contaminated with metals comparing to the Sundarbnn Mangrove Forest and Meghna water streams.

Table 3: Concentrations of Heavy Metals in Water Specimens Collected from the Location of Chilmari, Kurigram, Bangladesh

Standard Limit of Metals in Irrigation and Drinking Water													
Target Metals	**Pb, mg/L**	**Cd, mg/L**	**Cr, mg/L**	**Cu, mg/L**	**Co, mg/L**	**Ni, mg/L**	**Fe, mg/L**	**Mn, mg/L**	**Zn, mg/L**	**Ca**	**Mg**	**Na**	**K**
Irrigation	0.10 [a]	0.05 [a]	1.00 [a]	3.00[a]	0.05[b]	1.00 [a]	2.00 [a]	5.00 [a]	10.00 [a]	NC	NC	NC	NC
Drinking	0.05 [a]	0.005 [a]	0.001 [a]	1.00 [a]	0.05[b]	0.10 [a]	0.30-1.00 [a]	0.10 [a]	5.00 [a]	NC	NC	NC	NC
Concentration of Metals Observed in Water Specimens													
Water Samples	**Pb (μG/L)**	**Cd (μG/L)**	**Cr (μG/L)**	**Cu (μG/L)**	**Co (μG/L)**	**Ni (μG/L)**	**Fe (μG/L)**	**Mn (μG/L)**	**Zn (μG/L)**	**Ca (Mg/L)**	**Mg (Mg/L)**	**Na (Mg/L)**	**K (Mg/L)**
WS-1	37±0.26	<3.0	<4.0	10.3±0.1	<3.0	18.4±0.11	281±2.5	16.7±0.1	22.8±0.1	20.5±0.04	5.7±0.02	50.8±1.4	2.96±0.01
WS-2	<20.0	<3.0	<4.0	11.1±0.1	<3.0	22.6±1.0	506±3.5	24.8±0.2	10.1±0.4	19.2±0.04	4.9±0.01	46.6±0.4	1.83±0.01
WS-3	<20.0	<3.0	<4.0	3.9±0.1	<3.0	<3.0	414±0.8	<3.0	14.4±0.6	20.2±0.06	5.4±0.01	5.5±0.01	2.21±0.02
WS-4	<20.0	<3.0	<4.0	7.7±0.1	<3.0	3.8±0.2	468±4.2	5.1±0.1	13.8±0.8	19.5±0.06	6.8±0.01	4.5±0.02	1.80±0.01
Avg. conc.	37	ND	ND	8.25	ND	14.9	417.2	15.5	15.2	19.8	5.7	26.2	2.2

[a] Department of Environment (DoE) (2003) A Compilation of Environmental Laws, Department of Environment

and Bangladesh EnvironmentalManagement Project, Schedule 10.
[b]http://faolex.fao.org/docs/texts/mat52519.docaccessed on June 29, 2015, an website of Food and Agriculture Organization (FAO) of United Nation.NC – No concerned by different agencies and or no standard limit data available.ND – Not detected.

Soil Samples Analysis

Five soils were collected from the spots pf the lands where fruits and vegetables were cultivated.These samples were subjected and analyzed the concentration of metals including Pb, Cd, Cr, Cu, Co, Ni, Fe, Mn, Zn, Ca, Mg, Na and K.Table 4 summarizes the observed concentration of target metals in soil specimens.Irrespective of soil samples collection points, all target metals were detected in different concentration ranges.The Pb, Cd, Cr, Cu, Co, Ni, Mn, Zn and Mg were lower than the standard admissible levels.The obtained values ranged from 20 to 32 mg/kg for Pb, 0.4 to 0.6 mg/kg for Cd, 30 to 36 mg/kg for Cr, 27.2 to 41.6 mg/kg for Cu, 12.8 to 18.6 mg/kg for Co, 33.6 to 43.2 mg/kg for Ni, 299 to 476 mg/kg for Mn, 92.6 to 226.4 mg/kg for Zn and 8885 to 14258 mg/kg for Mg.In the case of Fe, the concentration was found as 18398 to 26063 mg/kg which is ~ 100 times higher than the standard levels in soil.The increased concentration of Fe in the

Table 4: Concentrations of Heavy Metals in Soil Collected from the Location of Chilmari, Kurigram, Bangladesh

Standard Limit of Metals in Soil Specimens													
Target Metals	**Pb (mg/Kg)**	**Cd (mg/Kg)**	**Cr (mg/Kg)**	**Cu (mg/Kg)**	**Co (mg/Kg)**	**Ni (mg/Kg)**	**Fe (mg/Kg)**	**Mn (mg/Kg)**	**Zn (mg/Kg)**	**Ca (mg/Kg)**	**Mg (mg/Kg)**	**Na (mg/Kg)**	**K (mg/Kg)**
Soil	250-500[c]	3-6[c]	200[d]	135-200[c]	20[e]	60[d]	75-150[c]	630[e]	300-600[c]	H[e]	325,000[e]	H[e]	H[e]
Concentration of Metals Observed in Soil Specimens													
Soil Samples	**Pb (mg/Kg)**	**Cd (mg/Kg)**	**Cr (mg/Kg)**	**Cu (mg/Kg)**	**Co (mg/Kg)**	**Ni (mg/Kg)**	**Fe (mg/Kg)**	**Mn (mg/Kg)**	**Zn (mg/Kg)**	**Ca (mg/Kg)**	**Mg (mg/Kg)**	**Na (mg/Kg)**	**K (mg/Kg)**
SB-1	30±0.7	0.6±0.06	36.4±0.1	41.6±0.2	17.0±0.5	43.2±0.8	25234±25	442±2.6	132.8±0.7	5454±32.7	14258±14.3	6234±56.1	5139±10.3
SB-2	32±2.1	0.6±0.07	36.4±1.1	38.6±0.1	18.6±0.4	42.8±0.2	26063±104	476±3.3	92.6±2.1	5900±5.9	12935±12.9	1221±18.3	3912±31.3
SB-3	20±0.9	0.4±0.02	32.4±0.1	27.2±0.1	12.8±0.3	33.6±1.2	18398±110	299±0.3	226.4±0.9	5002±15	8885±26.7	929±3.7	3025±3.0
SB-4	28±1.0	0.6±0.05	36.4±0.3	38.6±0.2	16.2±1.0	40.6±0.1	23152±46	385±0.8	124.2±1.4	5214±10.4	11642±81.5	2365±14.2	3708±51.9
SB-5	24±0.9	0.6±0.03	30.0±0.1	31.8±0.4	14.0±0.1	37.2±1.4	20058±261	331±1.7	123.2±0.1	5936±23.7	9563±38.3	932±1.9	3254±3.2
Avg. conc.	26.7	0.48	34.7	35.3	15.7	39.4	22581	386.6	119.84	5501.2	11456.6	2336.2	3807.6

[c]Awashthi S.K. (2000):Prevention of Food Adulteration Act No. 37 of 1954. Central and State Rules asAmended for 1999; Ashoka Law House: New Delhi, India, p2000.
[d]SEPA, (2005):The Limits of Pollutants in Food; GB2762-2005; State Environmental Protection Administration: Beijing, China.
[e]U.S. EPA- Maximum Allowable Concentrations of chemical constituents in uncontaminated soils used as fill material at regulated fill operations (35 Ill. Adm. Code 1100.Subpart F) Revised: August 27, 2012.
H represents this chemical is of no concern for soil ingestion and no data are available to assess other routes of exposure.

soil could be contribution from numerous sources.Example includes the use of iron content metal equipment and machineries by farmers during cultivation of lands for farming fruits and vegetables in soils.The Fe is most abundance metals in earth and majority of devices/heavy duty supplies are made of Fe.Moreover the increase concentration of Fe may also be due to poor drainage or permanently flooding state of the soil. This could be as a result of the accumulation of the metal from the leached top soils which were not taken-up by plants, or washed-off during the rainy season. It could also be due to non-volatilization of the metallic compounds in solution in the soil.Additionally Fe is not generally considered a soil pollutant because it a component of the hemoglobin.The presence of macro- and micro nutrients were as order of Fe > Mg > Ca > K > Na >Mn> Zn based on average concentration values.The mean concentration of trace and toxic elements were in the order of Ni > Cu > Cr >Pb> Co > Cd.Wong et al. (2002) demonstrated the concentration of Cu and Zn approximately similar or lower than this study.Although Amusan et al. (2003) exemplified similar concentration, Sharma et al. (2009) observed higher concentration of Pb and Cd in a study conducted at Agra, India.These depict that the Chilmari area farming soils did not get contaminated with irrigated water or majority portion of the metals leached out.

Vegetable Samples Analysis

The macro-, micronutrients and toxic elements in different vegetables collected from the Chilmari sites were analyzed.The vegetables grown (Fig. 2 and Table 1) were irrigated with Brahmaputra River were subjected in this study.Table 5 displays the concentration of the Pb, Cd, Cr, Cu, Co, Ni, Fe, Mn, Zn, Ca, Mg, Na and K in the five composite fruits/vegetables specimens**.**The Pb and Cd were not detected any five of the vegetables samples.The other metal concentrations were observed in the range of 16.4 – 26.2 mg/kg for Cr, 21.6 to 43.0 mg/kg for Cu, 48.2 – 52.2 mg/kg for Co, 72.0 – 122.2 mg/kg for Ni, 1134 - 1490 mg/kg for Fe, 23.0 - 50 mg/kg for Mn and 79.0 – 121mg/kg for Zn,915.0 – 8158.0 for Ca, 547 - 4181 mg/kg for Mg, 499.0 – 8158.0mg/kg for Na and 3903.0 – 17103.0 mg/kg for K.The Co concentration was obtained within the standard permissible limits of 50.0 to 115.0 mg/kg.The Zn and Cu concentrations

Table 5: Concentrations of Heavy Metals in Vegetables collected from the Location of Chilmari, Kurigram, Bangladesh

Standard Limit of Metals in Vegetables Specimens													
Target Metals	**Pb (mg/ Kg)**	**Cd (mg/ Kg)**	**Cr (mg/ Kg)**	**Cu (mg/ Kg)**	**Co (mg/ Kg)**	**Ni (mg/ Kg)**	**Fe (mg/ Kg)**	**Mn (mg/ Kg)**	**Zn (mg/ Kg)**	**Ca (mg/ Kg)**	**Mg (mg/ Kg)**	**Na (mg/ Kg)**	**K (mg/ Kg)**
Vegetables	0.5-30 [f]	<2.4 [f]	0.1-0.2 [g]	30 [f]	50-115 [h]	0.02-50 [f]	400-500 [f]	0.3 [x]	20-100 [f]	NC	NC	NC	NC
Concentration of Metals Observed in Vegetables Specimens													
Vegetables samples	**Pb (mg/ Kg)**	**Cd (mg/ Kg)**	**Cr (mg/ Kg)**	**Cu (mg/ Kg)**	**Co (mg/ Kg)**	**Ni (mg/ Kg)**	**Fe (mg/ Kg)**	**Mn (mg/ Kg)**	**Zn (mg/ Kg)**	**Ca (mg/ Kg)**	**Mg (mg/ Kg)**	**Na (mg/ Kg)**	**K (mg/ Kg)**
VB-1	<20.0	<3.0	16.4±0.3	43.0 ±0.3	50.2 ±2.1	87.4±0.6	1298±1.3	33±0.3	121 ±2.8	8158 ±48.9	2934 ±5.9	1040 ±1.0	9436 ±9.4
VB-2	<20.0	<3.0	17.6±0.3	40.2 ±0.3	48.2 ±0.2	122.2 ±2.2	1134±23.0	26±0.3	113 ±1.4	4524 ±18.1	4181 ±8.4	3605 ±10.8	16905±16.8
VB-3	<20.0	<3.0	22.4±0.2	21.6 ±0.1	52.2 ±0.4	91.6±1.5	1165±1.2	24±0.2	79±1.0	1077 ±5.4	3161 ±22.1	8158 ±40.7	8106 ±218.8
VB-4	<20.0	<3.0	20.8±0.4	26.6 ±0.4	48.6 ±0.3	72±2.5	1207±3.6	23±0.1	106 ±0.7	915 ±1.8	547 ±2.2	499 ±7.9	3903 ±23.4
VB-5	<20.0	<3.0	26.2±0.2	35.8 ±0.1	49.2 ±0.1	82.2±2.1	1490±5.9	50±0.3	108 ±0.9	7701 ±46.2	3754 ±26.2	2602 ±46.8	17103±34.2
Avg. conc.	ND	ND	20.6	33.4	49.6	91.1	1238.8	31.2	105.4	4475	2915.4	3180.8	11090.6

[f]Opaluwa O. D., Aremu M. O., Ogbo L. O., Abiola K. A.,Odiba I. E.,Abubakar M. M.,Nweze N.O.(2012): FAO/WHO guidelines for metals in foods and vegetables.Heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis, Nasarawa State, Nigeria. Advances of Applied Science and Research,3 (2): 780-784.
[g] FAO/WHO guideline ; Akan J. C., AbdulrahmanF. I., Ogugbuaja V. O., Ayodele J. T. (2009): Heavy metals and anion levels in some samples of vegetables grown within the viciniy of Challawa Industrial area, Kano State, Nigeria. American Journal of Applied Sciences, 6:534-542.
ND – Not detected.
[h] Anderson A. J., Meyer R., Mayer F. K. (1973):Heavy metals toxicities: Levels of nickel, cobalt and chromium in the soil and plants associated with visual symptoms and variation of growth of an Oat crop. Australian Journal of Agriculture and Research, 24:557-571.
[x]ANSTAT (2001). Australia and New Zealand Food Standards Code, Vol. 2, Victoria.

were within admissible limit of 20-100 and 30 mg/kg respectively or border line high (Table 5).The increasing concentrations of Ni, Cr and Mn were observed in the samples specially at least 1 order of magnitude higher for Cr and Mn.Other groups reported the higher concentration of Pb, Cd and Cr in vegetables irrigated with water samples (Wang et al. 2005; Seid-mohammadi et al., 2014).The macro- and micronutrients were found in the order of K > Ca > Na > Mg > Fe >Mn> Zn and their values are higher concentration as expected because of healthy food habits requirement.Trace and toxic metals concentrations were observed as Ni > Co > Cu > Cr in this study.

Although vegetables are important source of minerals and fiber, consumption of metal contaminated vegetables may pose a risk to the human health and or animals over longer period of time.Taking contaminated vegetables may health hazardous consequences not limited to kidney and liver damage, skin rashes, stomach upset and ulcer, respiratory problems and lung cancer and alteration of genetic materials.Extreme metal contamination through dietary process beyond admissible limits may cause to nervous, cardiovascular, renal, neurological impairment as well as bone diseases and several other health disorders (Jolly et al. 2013; Jarup2003; Steenland and Boffetta2000).

Evaluation of Water, Soil and Vegetable Samples

Target metal concentrations in sampled water, soils and vegetables were evaluated based on the comparison of their average values and are represented in Table 6.In general it has been observed that maximum numbers of target metals were observed in soils following vegetables.The least number of metals were obtained in water samples.In majority instance, the higher concentrations of Pb, Cd, Cr, Cu, Fe, Mn, Zn, Ca and Mg were found in soil than vegetables and or water.In the case of vegetables, increasing concentrations of Co, Ni, Na and K were determined compared to soils and water.Irrespective of metals consideration, water samples provided least values.

Table 6: Comparison of Average Concentration of Soils, Vegetables and Brahmaputra River Water of Chilmari, Kurigram, Bangladesh

Samples	Pb, Mg/ Kg	Cd, Mg/ Kg	Cr, Mg/ Kg	Cu,Mg /Kg	Co,M g/Kg	Ni, Mg/K g	Fe, Mg/Kg	Mn, Mg/Kg	Zn, Mg/Kg	Ca, Mg/Kg	Mg, Mg/Kg	Na, Mg/Kg	K, Mg/Kg
Soils	26.7	0.48	34.7	35.36	15.7	39.4	22581	386.6	119.8	5501.2	11456.6	2336.2	3807.6
Vegetables	ND	ND	20.6	33.4	49.6	91.1	1238.8	31.2	105.4	4475	2915.4	3180.8	11090. 6
Water[ł]	37[*]	ND[*]	ND[*]	8.25[*]	ND[*]	14.9[*]	417.2[*]	15.5[*]	15.2[*]	19.8	5.7	26.2	2.2

[ł] Brahmaputra River,[*]ug/L

CONCLUSIONS

A series of metals such as Pb, Cd, Cr, Cu, Co, Ni, Fe, Mn, Zn, Ca, Mg, Na and K were targeted to examine the concentration in Brahmaputra River water, soils and different vegetables specimens from the Chilmari area of Bangladesh.In the case of water, the average concentrations of macro- and micro nutrients metals were observed in the order of Fe > Na > Ca >Mn> Zn > Mg > K and trace toxic elements were Ni > Cu.For soils, the order was Fe > Mg > Ca > K > Na >Mn>Zn based on average concentration values and for trace and toxic elements were Ni > Cu > Cr >Pb> Co > Cd.Vegetables specimens provided the concentration in the K > Ca > Na > Mg > Fe >Mn> Zn and their values were higher concentration as expected because of healthy food habits requirement.Moreover an order of Ni > Co > Cu > Cr was found in vegetables.Excepting minor pollution concern of Fe, Cr, Ni and Mn, all other metals in vegetables were observed within the permissible limit of international and national health regulatory authorities.

ACKNOWLEDGEMENTS

The author (s) would like to thank Head, Chemistry Division, Atomic Energy Center, Dhaka, Bangladesh for laboratory and equipment facilities for this project.The author (M. Abdul Mottaleb) also acknowledge the assistance of Director, Center for Innovation and Entrepreneurship, Northwest Missouri State University, Maryville, Missouri, USA for research collaboration and helpful cooperation during manuscript preparation.

REFERENCES

1. Agbozu, I. E., Ekweoz, I. K. E., Opuene, K., (2007). Survey of heavy metals in the catfish synodontisclarias. Int. J. Env. Sci. Technol., 4, 93 98.
2. Ajasa, A. M. O.; Bello, M. O.; Ibrahim, A. O.; Ogunwande, I. A.; Olawore, N. O., (2004).Heavy trace metals and macronutrients status in herbal plants of Nigeria. Food Chem., 85, 67-71.
3. Akcay, H.; Oguz, A.; Karapire, C., (2003).Study of heavy metal pollution and speciation in Buyak Menderes and Gediz River sediments.Water Res., 37, 813-822.
4. Alloway, B. J., (2004). Contamination of soils in domestic gardens and allotments: a brief overview. Land Cont. Reclam., 12, 179 -187.
5. Amusan, A. A.; Bada, S. B.; Salami, A. T., (2003). Effect of traffic density on heavy metal content of soil and vegetable along road side in Osun State, Nigera. West Afri. J. Appl. Ecol., 4 (1), 107-114.
6. Arif, I. A.; Khan, H. A.; Al-Homaidan, A. A.; Ahamed. A., (2011).Determination of Cu, Mn, Hg, Pb, and Zn in the outer tissue washings, outer tissues, and inner tissues of different vegetables using ICP-OES. Pol. J. Env. Studies. 20 (4), 835-841.
7. Arora, M.; Kiran, B.; Rani, S.; Rani, A.; Kaur, B.; Mittal, N. (2008) Heavy metal accumulation in vegetables irrigated with water from different sources. Food Chem., 111, 811-815.
8. Biasioli, M.; Grcman, H.; Kralj, T.; Madrid, F.; Diaz-Barrientos, E.; Ajmone-Marsan, F., (2007). Potentially toxic elements contamination in urban soils: a comparison of three European cities. J. Env. Qual., 36, 70-79.
9. Chojnacka, K.; Chojnacki, A.; Gorecka, H.; Gorecki, H., (2005). Bioavailability of heavy metals from polluted soils to plants. Sci. Tot. Env., 337, 175-182.
10. Dassenakis, M.; Scoullos, M.; Foufa, E.; Krasakopoulou, E.; Pavlidou, A.; Kloukiniotou, M., (1988). Effects of

multiple source pollution on a small Mediterranean River. Appl. Geochem., 13, 197-211.

11. Ghani, T. N. A.; Elchaghaby, G. A. F., (2007).Influence of operating conditions on theremoval of Cu, Zn, Cd and Pb ions from wastewater by adsorption. Int. J. Env. Sci. Technol., 4, 451-456.
12. Harikumar, P. S.; Nasir, U. P.; Rahman, M. P. M., (2009).Distribution of heavy metals in the core sediments of a tropical wetland system. Int. J. Env. Sci. Technol., 6, 225-232.
13. Henry M.; Spliethoff, R. G.; Mitchell, L. N.; Ribaudo, O. T.; Hannah A. S.; Virginia G.; Debra O., (2014). Lead in New York City community garden chicken eggs: influential factors and health implications. Env. Geoch. Health, 36, 633-649.
14. Husaini, S. N.; Zaidi, J. H.; Naeem, K.; Akram, M., (2011). Metal poisoning and human health hazards due to contaminated salad vegetables. J. Radioanal. Nucl. Chem., 287, 543–550.
15. Hobbelen, P. H. F.; Koolhaas, J. E.; van Gestel, C. A. M., (2009).Risk assessment of heavy metal pollution for detritivores in floodplain soils in the Biesbosch, the Netherlands, taking bioavailability into account.Env. Poll., 129, 409-419.
16. Jarup, L., (2003). Hazards of heavy metal contamination. British Med. Bull., 68,167–182.
17. Jolly, Y. N.; Islam, A.; Akbar, S., (2013).Transfer of metals from soil to vegetables and possible health risk assessment. SpringerPlus, 2:385, doi: 10.1186/2193-1801-2-385.
18. Khan, Y. S. A.; Hossain, M. S.; Hossain, S. M. G. A.; Halimuzzaman, A. H. M., (1998). An environmental assessment of trace metals in the Ganges- Brahmaputra-Meghna estuary. J Remed. Sanit. Env., 2, 103-117.
19. Marin, A.; Lopez-Gonzalvez, A.; Barbas, C., (2001).Development and validation of extraction methods for determination of zinc and arsenic speciation in soils using focused ultrasound: Application to heavy metal study in mud and soils.Anal. Chim. Acta, 442, 305-318.
20. McBride, M. B. ; Shayler, H. A.; Spliethoff, H. M.; Mitchell, R. G.; Marquez-Bravo, L. G. Ferenz, G. S.; Russell-Anelli, J. M.; Casey, L.; Bachman., S., (2014) Concentrations of lead, cadmium and barium in urban garden-grown vegetables: The impact of soil variables. Env. Poll., 194, 254-261.
21. Miller, C. V.; Foster, G. D.; Majedi, B. F., (2003).Baseflow and stormflow metal fluxes from two small agricultural catchments in the coastal plain of Chesapeake Bay Basin, United States.Appl. Geochem., 18, 483-501.
22. Mor F.; Ceylan S., (2008). Cadmium and lead contamination in vegetables collected from industrial, traffic and rural areas in Bursa Province, Turkey. FoodAddi. Contam**.** Part A, Chem. Anal. Cont.**,** Expo. Risk Assess.**,**25, 611.
23. Nicolau, R.; Galera-Cunha, A.; Lucas, Y., (2006). Transfer of nutrients and labile metals from the continent to the sea by a small Mediterranean river. Chemosphere, 63, 469-476.
24. Peralta-Videa, J. R.; Lopez, M. L.; Narayan, M.; Saupe, G.; Gardea-Torresdey, J., (2009). The biochemistry of environmental heavy metal uptake by plants: implications for the food chain. Int. J. Biochem. Cell Bio.,41, 1665.
25. Perello, G.; Marti-Cid, R.; Lobet, J. M.; Domingo, J. L., (2008). Effects of various cooking processes on the concentrations of arsenic, cadmium, mercury, and lead in foods. J. Agri. Food Chem., 56, 11262-11269.
26. Quraishi, S. B.; Choudhury,T. R.; Khan, S. R.; Mottaleb, M. A., (2010).Season- and year-wise distribution of some trace metals and anions in Gulshan Lake, Bangladesh. Maejo Int. J. Sci. Technol., 4(02), 337-346.
27. Rahman, M. T.; Rahman, M. S.; Quraishi, S. B.; Ahmad, J. U.; Choudhury, T. R.; Mottaleb, M. A., (2011).

Distribution of heavy metals in water and sediments in Passur River, Sundarban Mangrove Forest, Bangladesh.J. Int. Env. Appl. Sci., 6 (4), 537-546.

28. Seid-mohammadi, A.; Roshanaei, G.; Asgari, G., (2014).Heavy Metals Concentration in Vegetables Irrigated with contaminated and fresh water and estimation of their daily intakes in suburb areas of Hama-dan, Iran.J. Res. Health Sci., 14 (1) 69-74.
29. Sharma, S.; Prasad, F. M., (2009). Accumulation of lead and cadmium in soil and vegetable crops along major highways in Agra (India). J. Chem., 7(4), 1174-1183.
30. Sharma, R. K.; Agrawal, M.; Marshall, F. M., (2009). Heavy metals in vegetables collected from production and market sites of a tropical urban area of India. Food Chem. Toxicol., 47: 583–591.
31. Shrestha, R.; Fischer, R.; Sillanpaa, M., (2007). Investigations on different positions of electrodes and their effects on the distribution of Cr at the water sediment interface. Int. J. Env. Sci. Technol., 4, 413-420.
32. Shrivas, K.; Jaiswal, N. K., (2013). Dispersive liquid–liquid microextraction for the determination of copper in cereals and vegetable food samples using flame atomic absorption spectrometry. Food Chem., 141, 2263–2268.
33. Steenland, K.; Boffetta, P., (2000).Lead and cancer in humans: where are we now? Am. J. Ind. Med., 38, 295–299.
34. Stilwell, D. E.; Rathier, T. M.; Musante, C. L.; Ranciato, J. F., (2008). Lead and other heavy metals in community gardens soils in Connecticut (No. Bulletin 1019). The Connecticut Agricultural Experiment Station.
35. Radwan, M. A.; Salama, A. K., (2006). Market basket survey for some heavy metals in Egyptian fruits and vegetables. Food Chem. Toxicol., 44, 1273-1278.
36. Randjelovic, S. S.; Kostic, D. A.; Stojanovic, G. S.; Mitic, S. S.; Mitic, M. N.; Arsic, B. B.; Pavlovic, A. N., (2014). Metals content of soil, leaves and wild fruit from Serbia. Central Euro. J. Chem., 12(11), 1144-1151.
37. Wang, X.; Sato, T.; Xing, B.; Tao, S., (2005).Health risks of heavy metals to the general public in tianjin, China via consumption of vegetables and fish. Sci. Tot. Env.,350, 28-37.
38. Weigert P., (1991). Metal loads of food of vegetable origin including mushroooms. In: Merian E, (Eds.), Metals and their compounds in the environment: occurrence, analysis and biological relevance.VCH publisher Inc, Weinheim.
39. Wong, S. C.; Li, X. D.; Zhng, G.; Qi, S. H., (2002). Heavy metals in agricultural soils of the Pearl River Delta, South China. Env. Poll.,119, 33-44.
40. Zaidi, J. H.; Arif, M.; Fatima, I.; Qureshi I. H., (2002). Radiochemical neutron activation analysis for trace elements of basic ingredients of pan. J. Radioanal. Nucl. Chem., 253, 459-64.
41. Zvinowanda, C. M.; Okonkwo, J.O.; Shabalala, P. N.; Agyei, N. M., (2009).A novel adsorbent for heavy metal